

⑫

**EUROPEAN PATENT SPECIFICATION**

⑬ Date of publication of patent specification: **16.04.86**

⑭ Int. Cl.<sup>4</sup>: **C 11 D 3/20, C 11 D 3/50,**  
**C 11 D 17/00**

⑮ Application number: **82201396.7**

⑯ Date of filing: **08.11.82**

⑰ **Liquid detergent compositions.**

⑱ Priority: **12.11.81 GB 8134060**

⑲ Date of publication of application:  
**08.06.83 Bulletin 83/23**

⑳ Publication of the grant of the patent:  
**16.04.86 Bulletin 86/16**

㉑ Designated Contracting States:  
**BE DE FR GB IT NL**

㉒ References cited:  
**EP-A-0 040 882**  
**GB-A-1 308 190**  
**GB-A-1 603 047**

㉓ Proprietor: **THE PROCTER & GAMBLE**  
**COMPANY**  
**301 East Sixth Street**  
**Cincinnati Ohio 45202 (US)**  
㉔ **GB**

㉕ Proprietor: **Procter & Gamble European**  
**Technical Center**  
**Temselaan 100**  
**B-1820 Strombeek-Bever (BE)**  
㉖ **BE DE FR IT NL**

㉗ Inventor: **König, Axel**  
**117 De Ridderlaan**  
**B-1810 Wemmel (BE)**

㉘ Representative: **Ernst, Hubert et al**  
**PROCTER & GAMBLE EUROPEAN TECHNICAL**  
**CENTER Temselaan 100**  
**B-1820 Strombeek-Bever (BE)**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Courier Press, Leamington Spa, England.

**EP 0 080 749 B1**

**BEST AVAILABLE COPY**

## Description

### Technical field

This invention relates to aqueous detergent compositions suitable for use as general purpose household cleaning compositions.

### Background

General purpose household cleaning compositions for hard surfaces such as metal, glass, ceramic, plastic and linoleum surfaces, are commercially available in both powdered and liquid form. Powdered compositions consist mainly of builder or buffering salts such as phosphates, carbonates, silicates, etc., and although such compositions may display good inorganic soil removal, they are generally deficient in cleaning ability on organic soils such as the greasy/fatty/oily soils typically found in the domestic environment. Moreover, they are diluted with water prior to use.

Liquid cleaning compositions, on the other hand, have the great advantage that they can be applied to hard surfaces in neat or concentrated form so that a relatively high level of surfactant material is delivered directly to the soil. Moreover, it is a rather more straightforward task to incorporate high concentrations of anionic or nonionic surfactant in a liquid rather than a granular composition. For both these reasons, therefore, liquid cleaning compositions have the potential to provide superior grease and oily soil removal over powdered cleaning compositions.

Nevertheless, liquid cleaning compositions still suffer a number of drawbacks which can limit their consumer acceptability. Thus, they generally contain little or no detergency builder salts and consequently they tend to have poor cleaning performance on particulate soil and also lack "robustness" under varying water hardness levels. In addition, they can suffer problems of product form, in particular, inhomogeneity, lack of clarity, or inadequate viscosity characteristics for consumer use. Moreover, the higher in-product and in-use surfactant concentration necessary for improved grease handling raises problems of extensive suds formation, which require frequent rinsing and wiping by the user. Although oversudsing may be controlled to some extent by incorporating a suds-regulating material such as hydrophobic silica and/or silicone or soap, this in itself can raise problems of poor product stability and homogeneity, and problems associated with deposition of insoluble particulate or soap residues on the items or surfaces being cleaned, leading to filming, streaking and spotting.

It has now been discovered, however, that these defects of prior art liquid cleaning compositions can be minimized or overcome through the use therein of mono- or sesquiterpene material in combination with Butyl Carbitol (a Trademark for 2-(2-butoxyethoxy)ethanol). Although the said terpenes, have limited water-solubility, it has now been found that they can be incorporated into

liquid cleaning compositions in homogeneous form, even under "cold" processing conditions. The said terpenes provide excellent cleaning characteristics across the range of water hardness on grease/oily soils and inorganic particulate soils, as well as on shoe polish, marker ink, bath tub soil etc., and excellent shine performance with low soil redeposition and little or no propensity to cause filming, streaking or spotting on surfaces washed therewith. Moreover, the terpenes herein specified, and in particular those of the hydrocarbon class, are valuable in regulating the sudsing behaviour of the instant compositions in both hard and soft water and under both diluted and neat or concentrated usage, while terpenes of the terpene alcohol class are also valuable for providing effective control of product viscosity characteristics.

Terpenes are, of course, well-known components of perfume compositions and are often incorporated into detergent compositions at low levels via the perfume. Certain terpenes have also been included in detergent compositions at higher levels; for instance, DE—A—21 13 732 discloses the use of aliphatic and alicyclic terpenes as anti-microbial agents in washing compositions; GB—A—1,308,190 teaches the use of dipentenenes in a thixotropic liquid detergent suspension base composition. DE—A—27 09 690 teaches the use of pine oil (a mixture mainly of terpene alcohols) in liquid hard surface cleaning compositions. European Application 81-200540.3 (EP—A—0040882, published 2.12.81) teaches the use of mono- or sesquiterpenes with solvents such as benzyl alcohol and ethylene glycol dibutyl ether in liquid cleanser compositions.

The present invention provides liquid detergent compositions which are stable, homogeneous liquids having excellent suds control across a broad range of usage and water hardness conditions and which provide excellent shine performance together with improved cleaning characteristics both on greasy/oily soils and on inorganic particulate soils, with little tendency to cause filming or streaking on washed surfaces.

### Summary of the invention

According to the present invention there is provided an aqueous liquid detergent composition characterized by:

(a) at least 0.1% (preferably 1%—20%) of a synthetic anionic, nonionic, amphoteric or zwitterionic surfactant or mixture thereof;

(b) at least 0.5% (preferably 1%—10%) of a mono- or sesquiterpene or mixture thereof (most preferably the weight ratio of surfactant: terpene is in the range of 5:1 to 1:3) and

(c) at least 0.5% (preferably 0.5%—10%) of 2-(2-butoxyethoxy)ethanol.

### Detailed description of the invention

The essential terpene, Butyl Carbitol and surfactant components, and other optional ingredients, used in the practice of the present invention are described in more detail, hereinafter. All

percentages are by weight, unless otherwise specified.

#### Terpene

Preferred terpenes are monocyclic and bicyclic monoterpenes, especially those of the hydrocarbon class, which include the terpinenes, terpeneolens, limonenes and pinenes, and mixtures thereof. Highly preferred materials of this type are d-limonene, dipentene,  $\alpha$ -pinene,  $\beta$ -pinene and the mixture of terpene hydrocarbons obtained from the essence of oranges (e.g. cold-pressed orange terpenes and orange terpene oil phase ex fruitjuice). These terpenes are used at concentrations of at least 0.5%, preferably 1% to 10%, most preferably 2%—6%, in the compositions.

Terpene alcohols, aldehydes and ketones can optionally be used, but are not as preferred as the terpenes noted above. The terpene alcohols do provide valuable and unexpected improvements in viscosity regulation when incorporated in the compositions of this invention at concentrations from 1% to 3%, more preferably from 1.5% to 2.5%.

#### Butyl Carbitol (Registered Trademark)

This component of the present compositions is commercially available as 2-(2-butoxyethoxy)-ethanol, and is otherwise known as diethylene glycol monobutyl ether ( $C_8H_{18}O_3$ ). Butyl Carbitol is used in the present compositions at a concentration of at least 0.5%, preferably from 0.5% to 10%, by weight of composition. Butyl Carbitol has unexpected advantages over solvents like benzyl alcohol: it has none of the cloying odor associated with benzyl alcohol and oxidation products thereof; it performs well as a grease remover; it acts, at least partially, as a hydrotrope, thereby allowing lower levels of hydrotropes like cumene sulfonate to be used in the present compositions.

#### Surfactants

Water-soluble deterative surfactants useful herein include well-known synthetic anionic, nonionic, amphoteric and zwitterionic surfactants. Typical of these are the alkyl benzene sulfates and sulfonates, paraffin sulfonates, olefin sulfonates, alkoxyated (especially ethoxyated) alcohols and alkyl phenols, amine oxides,  $\alpha$ -sulfonates of fatty acids and of fatty acid esters, and the like, which are well-known from the detergency art. In general, such deterative surfactants contain an alkyl group in the  $C_{10}$ — $C_{18}$  range; the anionic deterative surfactants are most commonly used in the form of their sodium, potassium or triethanolammonium salts; the nonionics generally contain from 3 to 17 ethylene oxide groups. U.S. Patents 4,111,855 and 3,995,669 contain detailed listings of such typical deterative surfactants.  $C_{12}$ — $C_{18}$  alkyl benzene sulfonates and  $C_{12}$ — $C_{18}$  paraffin-sulfonates are especially preferred in the compositions of the present type.

The surfactant component can comprise as little as 0.1% of the compositions herein when formulated as a spray-on type product. When formulated as standard liquid cleaners, the compositions herein generally will contain 1% to 20%, preferably 2% to 8%, of surfactant.

#### Optional ingredients

The compositions herein can contain other ingredients which aid in their cleaning performance. For example, it is highly preferred that the compositions contain a detergent builder and/or metal ion sequestrant. Compounds classifiable and well-known in the art as detergent builders include the nitrilotriacetates, polycarboxylates, citrates, water-soluble phosphates, mixtures of ortho- and pyro-phosphates, zeolites, especially hydrated zeolite A in the 1—10 micrometer particle size range, and mixtures thereof. Metal ion sequestrants include all of the above, plus materials like ethylenediaminetetraacetate, the amino-polyphosphonates and phosphates (Dequest®) and a wide variety of other poly-functional organic acids and salts too numerous to mention in detail here. See U.S. Patent 3,579,454 for typical examples of the use of such materials in various cleaning compositions. In general, the builder/sequestrant will comprise 1% to 25% of the composition. Of course, water-soluble builder/sequestrants are used if clear, homogeneous compositions are desired. Citric acid (2%—10% as sodium citrate) is preferred herein.

#### Soaps

As mentioned hereinabove, one special problem associated with the use of liquid cleansers is their tendency to over-suds, in-use. It has been discovered that soaps, especially the alkali, ammonium and alkanolammonium salts of  $C_{13}$ — $C_{24}$  fatty acids, are especially useful as suds suppressors when conjointly present with terpenes and Butyl Carbitol in the instant compositions. Soap concentrations of at least 0.005%, preferably 0.05% to 2%, provide this important suds control function. Soap prepared from coconut oil fatty acids is preferred.

#### Thickeners

The compositions herein may optionally be thickened. Thickened compositions tend to cling to vertical surfaces such as walls and windows, which makes them more convenient to use. It has been found that many common thickeners undesirably flocculate the compositions herein. However, it has been discovered that thickeners based on Xanthan polysaccharides are effective, non-flocculating thickeners. In general, such Xanthan thickeners are used herein at levels of 0.01% and higher, depending on the desires of the formulator.

Moreover, the compositions herein can contain, in addition to ingredients already mentioned, various optional ingredients typically used in commercial products to provide aesthetic or additional product performance benefits. Typical

ingredients include pH regulants, perfumes, dyes, optical brighteners, soil suspending agents, detergent enzymes, gel-control agents, freeze-thaw stabilizers, bactericides, preservatives and the like.

Another additional ingredient for use herein is represented by conventional detergent hydrotropes. Examples of suitable hydrotropes are urea, monoethanolamine, diethanolamine, triethanolamine and the sodium, potassium, ammonium and alkanol ammonium salts of xylene-, toluene-, ethylbenzene- and isopropylbenzene sulfonates. These hydrotropes can be added to the compositions of the present invention in amounts up to 10% by weight. It is a particular feature of the present invention, however, that stable, homogeneous formulations can be prepared without the need for hydrotropic materials of this kind, or with only very minor levels such as amount of from 0 to 4% (up to 4%) by weight.

The compositions herein are formulated in the alkaline pH range, generally in the range of pH 8—11, preferably 10—10.8. Caustics such as sodium hydroxide and sodium carbonate can be used to adjust and buffer the pH, as desired.

Since the compositions herein are in liquid form, they can be prepared by simply blending the essential and optional ingredients in water.

The following examples are given by way of illustrating the compositions herein, but are not intended to be limiting of the scope of the invention.

5

10

15

20

25

30

35

40

45

50

55

60

65

4

## Example I

Ingredient	Percent
Sodium C <sub>12-14</sub> alkyl benzene sulfonate	5.2
Sodium nitrilotriacetate	4.5
$\alpha$ -Pinene	10.1
Butyl Carbitol	10.1
Cumene sulfonate	1.8
Sodium hydroxide	4.1
Perfume and dye	0.2
Water	Balance

The composition of Example I exhibits excellent grease removal from asphalt tile when applied neat, or as a 1—15% aqueous solution. Excessive sudsing is not a problem if usage concentrations are below 10% in water.

BEST AVAILABLE COPY

Example II	
Ingredient	Percent
Sodium paraffin sulfonate	4.0
Orange terpenes	2.0
Butyl Carbitol	1.5
Sodium citrate	3.0
Sodium coconut soap	0.3
Cumene sulfonate	1.8
Sodium carbonate	5.0
Xanthan gum	0.1
Perfume	0.2
Water	Balance

The composition of Example II exhibits good freeze-thaw stability, an excellent low suds profile, excellent odor quality and has a desirable viscosity in the range of  $0.15 \text{ g.cm}^{-1}.\text{s}^{-1}$ . The product is conveniently used neat, or in a 1–50% aqueous solution, to remove all manner of greasy oily stains from hard surfaces.

Example III	
Ingredient	Percent
Alkyl benzene sulfonate (Na)	3.0
Ethoxylated (E07) coconut alcohols	3.0
Dimethyldodecylamine oxide	2.0
$\alpha$ -pinene	0.2
$\beta$ -pinene	0.2
d-limonene	0.4
Dipentene	0.4
Pine oil	0.1
Sodium coconut soap	0.45
Cumene sulfonate	1.2
Sodium nitrilotriacetate	2.0
Sodium tripolyphosphate	1.5
Butyl Carbitol	3.0
Water	Balance
NaOH	to pH 10.6

The composition of Example III is prepared as a fully-formulated liquid cleanser suitable for use in water in the hardness range of 0.12 to 0.22 gram per liter. The composition provides excellent removal of both greasy and solid soils from all manner of surfaces.

#### Claims

1. An aqueous liquid detergent composition comprising:

(a) at least 0.1% by weight of a surfactant selected from synthetic anionic, nonionic, amphoteric and zwitterionic surfactants and mixtures thereof;

(b) at least 0.5% by weight of a mono or sesquiterpene or mixture thereof; and

(c) at least 0.5% by weight of 2-(2-butoxyethoxy)ethanol.

2. A composition according to Claim 1 wherein the surfactant is selected from the alkyl benzene-sulfonates, paraffin sulfonates, olefin sulfonates, ethoxylated alcohols, ethoxylated alkyl phenols, amine oxides, alpha-sulfonated fatty acids and esters thereof, and mixtures thereof.

3. A composition according to Claim 1 or 2 wherein the terpene is a monocyclic bicyclic monoterpene selected from the terpinenes, terpinolenes, limonenes, and pinenes and mixtures thereof.

4. A composition according to Claim 3 wherein the terpene is selected from d-limonene, dipentene, alpha-pinene and beta-pinene.

5. A composition according to Claim 1 or 2 wherein the terpene is a terpene alcohol, terpene aldehyde or terpene ketone.

6. A composition according to Claim 1, 2, 3, 4 or 5, which comprises from 0.5% by weight to 10% by weight of 2-(2-butoxyethoxy)ethanol.

7. A composition according to Claim 6, comprising from 1% to 20% by weight of the surfactant which is selected from alkyl benzene sulfonate and paraffin sulfonate, and from 1% to 25% by weight of a detergent builder or metal ion sequestrant.

8. A composition according to Claim 7 wherein the builder is selected from the water-soluble salts of citric acid, nitrilotriacetic acid, tripolyphosphate, or mixtures thereof.

9. A composition according to any of Claims 1 through 8, comprising at least 0.005% by weight of an alkali metal, ammonium or alkanol-ammonium soap of a  $\text{C}_{13}$  to  $\text{C}_{24}$  fatty acid.

10. A composition according to Claim 9 which comprises from 0.05% to 2% by weight of the soap of coconut fatty acids.

11. A composition according to any one of Claims 1–10, thickened with a Xanthan polysaccharide.

12. A composition according to any one of Claims 1–10 which in addition contains a hydro-trope in a level up to 4% by weight.

### Patentansprüche

1. Ein wäßriges flüssiges Wasch- und Reinigungsmittel enthaltend:

(a) mindestens 0,1 Gew.-% eines Tensids ausgewählt aus synthetischen anionischen, nichtionischen, amphoteren und zwitterionischen Tensiden und Gemischen davon;

(b) mindestens 0,5 Gew.-% eines Mono- oder Sesquiterpens oder Gemische davon; und

(c) mindestens 0,5 Gew.-% 2-(2-Butoxyethoxy)-ethanol.

2. Ein Mittel nach Anspruch 1, worin das Tensid ausgewählt ist aus den Alkylbenzolsulfonaten, Paraffinsulfonaten, Olefinsulfonaten, ethoxylierten Alkoholen, ethoxylierten Alkylphenolen, Aminoxyden,  $\alpha$ -sulfonierten Fettsäuren und Estern davon und Gemischen davon.

3. Ein Mittel nach Anspruch 1 oder 2, worin das Terpen ein monocyclisches oder bicyclisches Monoterpen ist, ausgewählt aus den Terpinen, Terpinolenen, Limonenen und Pinenen und Gemischen davon.

4. Ein Mittel nach Anspruch 3, worin das Terpen ausgewählt ist aus d-Limonen, Dipenten,  $\alpha$ -Pinen und  $\beta$ -Pinen.

5. Ein Mittel nach Anspruch 1 oder 2, worin das Terpen ein Terpenalkohol, Terpenaldehyd oder Terpenketon ist.

6. Ein Mittel nach Anspruch 1, 2, 3, 4 oder 5, das 0,5 bis 10 Gew.-% 2-(2-Butoxyethoxy)ethanol enthält.

7. Ein Mittel nach Anspruch 6, enthaltend 1 bis 20 Gew.-% des Tensids, das ausgewählt ist aus Alkylbenzolsulfonat und Paraffinsulfonat, und 1 bis 25 Gew.-% eines Detergensgerüststoffs oder Metallionensequestrierungsmittels.

8. Ein Mittel nach Anspruch 7, worin der Gerüststoff ausgewählt ist aus den wasserlöslichen Salzen von Zitronensäure, Nitrilotriessigsäure, Tripolyphosphat oder Gemischen davon.

9. Ein Mittel nach einem der Ansprüche 1 bis 8, enthaltend mindestens 0,005 Gew.-% einer Alkali-metall- Ammonium- oder Alkanolammonium-seife einer  $C_{13}$ -bis  $C_{24}$ -Fettsäure.

10. Ein Mittel nach Anspruch 9, das 0,05 bis 2 Gew.-% der Seife von Kokosnußfettsäuren enthält.

11. Ein Mittel nach einem der Ansprüche 1 bis 10, das mit einem Xanthanpolysaccharid verdickt ist.

12. Ein Mittel nach einem der Ansprüche 1 bis 10, das zusätzlich ein Hydrotrop in einer Menge bis zu 4 Gew.-% enthält.

### Revendications

1. Composition détergente liquide aqueuse — comprenant

(a) au moins 0,1% en poids d'un tensioactif choisi parmi les tensioactifs synthétiques anioniques, nonioniques, amphotères et zwitter-ioniques, et leurs mélanges;

(b) au moins 0,5% en poids d'un mono- ou sesquiterpène ou leurs mélanges; et

(c) au moins 0,5% en poids de 2-(2-butoxy-éthoxy)éthanol.

2. Composition selon la revendication 1, dans laquelle le tensioactif est choisi parmi les alkylbenzènesulfonates, les paraffinesulfonates, les oléfinesulfonates, les alcools éthoxylés, les alkylphénols éthoxylés, les oxydes d'amine, les acides gras  $\alpha$ -sulfonés et leurs esters, et leurs mélanges.

3. Composition selon la revendication 1 ou 2, dans laquelle le terpène est un monoterpène monocyclique ou bicyclique choisi entre les terpinènes, les terpinolènes, les limonènes, les pinènes et leurs mélanges.

4. Composition selon la revendication 3, dans laquelle le terpène est choisi entre le d-limonène, le dipentène, l' $\alpha$ -pinène et le  $\beta$ -pinène.

5. Composition selon la revendication 1 ou 2, dans laquelle le terpène est un alcool terpénique, un aldéhyde terpénique ou une cétone terpénique.

6. Composition selon la revendication 1, 2, 3, 4 ou 5, qui comprend de 0,5% à 10% en poids de 2-(2-butoxyéthoxy)éthanol.

7. Composition selon la revendication 6, qui comprend de 1 à 20% en poids du tensioactif, qui est choisi entre les alkylbenzènesulfonates et les paraffinesulfonates, et de 1 à 25% en poids d'un adjuvant pour détergent ou d'un séquestrant pour ion métallique.

8. Composition selon la revendication 7, dans laquelle l'adjuvant est choisi parmi les sels solubles dans l'eau de l'acide citrique, de l'acide nitrilotriacétique, les tripolyphosphates ou leurs mélanges.

9. Composition selon l'une quelconque des revendications 1 à 8, comprenant au moins 0,005% en poids d'un savon sel de métal alcalin, d'ammonium ou d'alkanol-ammonium d'un acide gras en  $C_{13}$  à  $C_{24}$ .

10. Composition selon la revendication 9, qui comprend de 0,05 à 2% en poids du savon d'acides gras dérivés de l'huile de coprah.

11. Composition selon l'une quelconque des revendications 1 à 10, épaissies par un polysaccharide dérivée de la gomme de xanthane.

12. Composition selon l'une quelconque des revendications 1 à 10, qui contient en outre un hydrotrope à une concentration allant jusqu'à 4% en poids.